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13. ABSTRACT (Maximum 200 words)

THE ROCKY MOUNTAIN ARSENAL REQUESTED THAT THE USGS CONDUCT A DIGITAL-MODEL STUDY OF THE DIMP CONTAMINATION OF GROUND WATER ON THE ARSENAL AND SURROUNDING PROPERTY IN ORDER TO PROVIDE INSIGHT INTO THE MECHANISM OF DIMP TRANSPORT AND TO PROVIDE DATA USEFUL IN MEETING THE REQUIREMENTS OF CEASE AND DESIST ORDERS. IN PARTICULAR, INFORMATION IS NEEDED CONCERNING THE AREA AFFECTED, CONCENTRATIONS, AND RATE AND DIRECTION OF MOVEMENT OF THE PLUME OF CONTAMINATED GROUND WATER. IF BRIGHTON'S MUNICIPAL WELL FIELD WILL BE AFFECTED, THE MODEL MAY BE USED TO DETERMINE FUTURE ARRIVAL TIMES AND CONCENTRATIONS. THE STUDY IS BEING UNDERTAKEN IN TWO PHASES. PHASE I INVOLVES THE CONVERSION OF THE EXISTING CHLORIDE TRANSPORT MODEL OF THE ARSENAL TO A DIMP TRANSPORT MODEL IN ORDER TO EVALUATE THE MAGNITUDE OF THE GROUND WATER CONTAMINATION IN THE IMMEDIATE AREA OF THE ARSENAL. PHASE II INVOLVES BUILDING A SECOND DIMP TRANSPORT MODEL OF A LARGER AREA IN ORDER TO INVESTIGATE THE POTENTIAL OF DIMP MOVING INTO BRIGHTON'S WELL FIELD AND OTHER ADJACENT AREAS. THIS REPORT DOCUMENTS THE RESULTS OF PHASE

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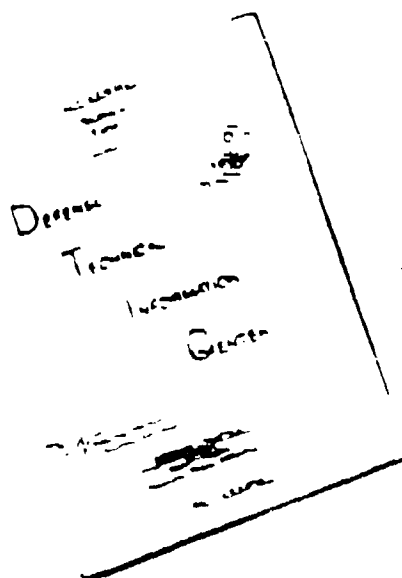
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✓ MODEL STUDY OF DIISOPROPYLMETHYLPHOSPHONATE
(DIMP) CONTAMINATION, ROCKY MOUNTAIN
ARSENAL NEAR DENVER, COLORADO
PROGRESS REPORT -- PHASE I

By S. G. Robson
U.S. Geological Survey

Prepared for the
U.S. DEPARTMENT OF THE ARMY,
ROCKY MOUNTAIN ARSENAL

Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

ADMINISTRATIVE REPORT

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Denver, Colorado

February 1976

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CONTENTS

	Page
Abstract.	1
Introduction.	1
Historical background of the contamination problem	1
Purpose and scope.	2
Acknowledgments.	3
Model development	3
Model calibration	5
Preliminary model projections	18
Management objectives	23
Summary	23
References.	24

ILLUSTRATIONS

Plate	1. Map showing Phase I model grid, location of recharge and discharge nodes, and steady-flow water-table contours, Rocky Mountain Arsenal and vicinity near Denver, Colorado.	In pocket
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		Page
Figures 1-9.	Maps showing:	
	1. Modeled transmissivity of the alluvial aquifer.	4
	2. May-July 1975 concentration of DIMP in ground water	8
	3. Model-generated 1975 concentration of DIMP in ground water.	9
	4. Model-calculated ground-water velocities.	10
	5. Model-generated 1956 concentration of DIMP in ground water.	12
	6. Model-generated 1960 concentration of DIMP in ground water.	13
	7. Model-generated 1964 concentration of DIMP in ground water.	14
	8. Model-generated 1968 concentration of DIMP in ground water.	15
	9. Model-generated 1972 concentration of DIMP in ground water.	16
10.	Graph showing change in DIMP concentration with time in selected wells.	17
11-14.	Maps showing:	
	11. Model-generated 1985 concentration of DIMP in ground water.	19
	12. Model-generated 1995 concentration of DIMP in ground water.	20
	13. Model-generated 1985 concentration of DIMP in ground water with ground-water barrier south of pond C	21
	14. Model-generated 1995 concentration of DIMP in ground water with ground-water barrier south of pond C	22

TABLE

	Page
Table 1. Recharge, discharge, and concentration of DIMP data for Phase I DIMP model.	6

METRIC CONVERSION FACTORS

<i>To convert English units</i>	<i>Multiply by</i>	<i>To obtain metric units</i>
acres	4.047×10^{-3}	square kilometres (km ²)
cubic feet per second (ft ³ /s)	28.32	litres per second (l/s)
feet (ft)	.3048	metres (m)
miles (mi)	1.609	kilometres (km)
square miles (mi ²)	2.590	square kilometres (km ²)
tons	.9072	tonnes (t)
feet per day (ft/d)	.3048	metres per day (m/d)

One microgram per litre (µg/l) is approximately equal to one part per billion. One milligram per litre is equal to 1,000 micrograms per litre and is approximately equal to one part per million.

Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

MODEL STUDY OF DIISOPROPYLMETHYLPHOSPHONATE (DIMP) CONTAMINATION,
ROCKY MOUNTAIN ARSENAL NEAR DENVER, COLORADO
PROGRESS REPORT -- PHASE I

By S. G. Robson

ABSTRACT

Diisopropylmethylphosphonate (DIMP) is an organic compound produced as a byproduct of manufacture and detoxification of a GB nerve gas agent that appears to function as a nonreactive tracer in the ground-water environment. A combination of ground-water and surface-water transport has spread the compound through large areas of a shallow alluvial aquifer near the Rocky Mountain Arsenal.

A ground-water solute transport model has been used to simulate DIMP concentrations in the alluvial aquifer. The Phase I model is the first and smaller of two models to be built in order to evaluate the effectiveness of various ground-water quality management alternatives. The model covers an area of about 30 square miles (77.7 square kilometres) and was calibrated primarily by comparison of simulated and observed 1975 DIMP concentrations. Two preliminary 20-year model projection runs were made to demonstrate the predictive ability of the model. The results of the larger Phase II model and the final model projections will be presented in a forthcoming final report.

INTRODUCTION

Historical Background of the Contamination Problem

The Rocky Mountain Arsenal was established in 1942 and presently encompasses about 27 mi² (70 km²) immediately northeast of the city of Denver, Colo. The northern boundary of the arsenal is about 7 mi (11 km) south of the city of Brighton, Colo. The arsenal was constructed to produce toxic chemical and incendiary munitions--about 242,000 tons (220,000 t) of which were manufactured during World War II (Reynolds, 1975). After a postwar reduction in activities, the arsenal began in 1953 a second manufacturing phase, upon completion of a new toxic chemical agent facility. This manufacturing and filling facility manufactured a GB nerve gas agent from 1953 to 1957. One byproduct of this manufacturing process was the organic compound diisopropylmethylphosphonate (DIMP). The arsenal has subsequently been involved in manufacturing anticrop agents and removing toxic chemicals from munitions. From 1973 to the present (1975) the GB manufacturing facility has been used to detoxify the GB agent held in bulk storage and in bombs and warheads.

The manufacturing and detoxification activities at the arsenal have produced industrial effluents, some of which have high dissolved-solids concentration and (or) high concentrations of organic compounds. Prior to 1956 these effluents were disposed of in unlined surface ponds. Effluent percolating through the bottom of these ponds has degraded the chemical quality of the ground water in a shallow alluvial aquifer. Subsequent to 1956 industrial effluents have been discharged to a lined reservoir (Reservoir F) and the unlined ponds have been either unused or used temporarily to hold surface runoff or fresh water.

Petri and Smith (1956) studied the ground-water quality near the arsenal in 1955 and 1956. They found that high concentrations of sodium and chloride in the aquifer extended from near the arsenal disposal ponds northwest to the South Platte River. Data from this and subsequent work were used by Konikow (1975a) to prepare detailed maps of the bedrock surface elevation, water-table elevation, and aquifer saturated thickness and transmissivity near the arsenal. Konikow later expanded this work to include a digital ground-water-quality model capable of simulating the movement and dispersion of chloride in the aquifer (Konikow, 1975b).

In 1974, DIMP was detected in ground water on the arsenal and surrounding property to the north and west. Trace concentrations were detected in wells as much as 7 mi (11 km) downgradient from the arsenal disposal ponds and within 1.0 mi (1.6 km) of two wells in the city of Brighton's municipal well field (pl. 1). Concern has been expressed about DIMP in potable ground water because little is known about toxicity levels or the effect of long-term consumption of trace amounts of the compound. This and an associated problem of ground-water contamination by a pesticide byproduct led the Colorado Department of Health to issue Cease and Desist Orders against the Rocky Mountain Arsenal and the Shell Chemical Co. The Shell Chemical Co. plant on the arsenal property is thought to be the source of the ground-water contamination by the pesticide byproduct dicyclopentadiene (DCPD). The Cease and Desist Orders state, in general, that the Rocky Mountain Arsenal and the Shell Chemical Co. are to:

1. Immediately stop the off-post discharge of DIMP and DCPD from both surface- and ground-water flow.
2. Submit a proposed plan of action to preclude such future off-post discharge and take action on the approved plan.
3. Develop and institute a surveillance plan to verify compliance with items 1 and 2.

Purpose and Scope

The Rocky Mountain Arsenal requested that the U.S. Geological Survey conduct a digital-model study of the DIMP contamination of ground water on the arsenal and surrounding property in order to provide insight into the mechan-

ism of DIMP transport and to provide data useful in meeting the requirements of Cease and Desist Orders. In particular, information is needed concerning the area affected, concentrations, and rate and direction of movement of the plume of contaminated ground water. If Brighton's municipal well field (pl. 1) will be affected, the model may be used to determine future arrival times and concentrations.

The study is being undertaken in two phases. Phase I involves the conversion of the existing chloride transport model (Konikow, 1975b) of the arsenal to a DIMP transport model in order to evaluate the magnitude of the ground-water contamination in the immediate area of the arsenal. Phase II involves building a second DIMP transport model of a larger area in order to investigate the potential for DIMP moving into Brighton's well field and other adjacent areas. Both models will assume conservative (nonreactive) transport of DIMP and will be calibrated using present data on DIMP concentrations in the aquifer. This report documents the results of Phase I. A subsequent report will document the work done on Phase II.

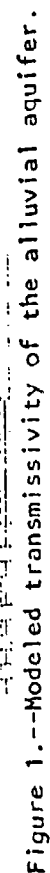
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Existing data on the DIMP concentrations in ground and surface waters were furnished by the Rocky Mountain Arsenal. These data included analyses run by the Colorado Department of Health, Shell Chemical Co., and the Rocky Mountain Arsenal. The arsenal also ran DIMP analyses on supplemental samples collected by the U.S. Geological Survey.

MODEL DEVELOPMENT

The model used for both the chloride and DIMP transport studies at the arsenal is based on an iterative alternating-direction implicit mathematical solution of the ground-water flow equations coupled with a method of characteristics solution of the solute transport equations as described by Bredehoeft and Pinder (1973). These mathematical procedures require that the area modeled be divided into numerous small rectangular segments or nodes of equal dimensions. In the Phase I model a 1,000-ft (300-m) interval grid was used to delineate the nodes (pl. 1). At each node in the area to be modeled the geohydrologic and chemical characteristics of the aquifer are described.

The geohydrologic characteristics of the alluvial aquifer near the arsenal have been described by Konikow (1975a). In general, he found that the direction of ground-water movement is from the southeast to northwest toward the South Platte River (pl. 1), and that the saturated thickness of the alluvial aquifer ranges from 0 to 60 ft (0 to 18 m). The aquifer is discontinuous 2 to 3 mi (3 to 5 km) east of the South Platte River because numerous bedrock highs separate areas in which the alluvium is saturated. In this area the direction of ground-water movement is controlled by the configuration of the aquifer. The transmissivity of the aquifer near Reservoir F is about $3,000 \text{ ft}^2/\text{d}$ ($280 \text{ m}^2/\text{d}$), which is about 7 times lower than the transmissivity near the river (fig. 1).



Water-level hydrographs for wells north and west of the arsenal show that there have been minimal long-term water-level changes in the area between 1937 and 1975 (Brookman, 1969). The most significant short-term water-level change occurred during the 1954-57 drought when water levels declined 3 to 5 ft (0.9 to 1.5 m). For modeling purposes, the ground-water system was assumed to be in a steady-flow condition from the time of DIMP discharge (1952-56) to the present (1975). To simulate these conditions, a steady-state flow model was coupled with a transient-state transport model. This modeling procedure enabled the simulation of the steady ground-water flow system in conjunction with aquifer DIMP concentrations that change during the 1952-75 simulation period.

The boundary conditions for the DIMP model were handled in the same manner as were those for the chloride model (Konikow, 1975b). Boundaries traversing the aquifer were modeled as constant-head boundaries; that is, boundaries at which the rate of flow across the boundary may vary but the head at the boundary is held constant. No-flow boundaries were simulated between the aquifer and the bedrock outcrops. Although the bedrock is known to contain permeable zones (McCcnaghy and others, 1964), the hydraulic conductivity of these zones is generally much less than that of the alluvium. As a result, the assumption of impermeable model boundaries is thought to be valid. This assumption is further substantiated by the successful model simulation.

The quantity and distribution of recharge and discharge to the DIMP model were similar to those used in the chloride model (pl. 1 and table 1), with one exception. Industrial effluent high in chloride was disposed into ponds A through E from about 1943 to 1956. Effluent containing DIMP was thought to be disposed into ponds A through E from 1952 to 1956. Unfortunately, no information is available on the concentration of DIMP in the effluent. As a result, the DIMP source concentrations used in the model were determined by trial and error as those which produced the best agreement between the 1975 field data and the corresponding model calculations.

The model assumes that conservative (nonreactive) ground-water transport and dispersion of DIMP will occur as the contaminant moves through the aquifer. In the absence of test data, it can only be assumed that DIMP is conservative; that is, it does not adsorb on the soil clay matrix, combine with other compounds, or undergo oxidation or reduction as it moves through the aquifer. This assumption appears to be valid when the concentration distributions of DIMP and the conservative tracer chloride are compared and is further substantiated by the fact that the same transverse and longitudinal dispersivity (100 ft or 30 m) proved adequate in both the chloride and DIMP models.

MODEL CALIBRATION

A calibration procedure was used to check the validity of the DIMP transport model. Calibration involved a comparison of (1) The observed water-table elevations with model-calculated water-table elevations, and (2) observed mid-1975 DIMP concentrations with the model-calculated 1975 DIMP concentrations. The agreement between the observed and calculated quantities is indicative of

Table 1.--Recharge, discharge, and concentration of DIMP data for Phase I DIMP model

Source ¹	1952-75 average		Average DIMP		
	recharge or discharge,		concentration,		
	in cubic feet per second		in micrograms per litre		
	Recharge	Discharge	1952-56	1956-74	1974-75
A	0.072	-	17,000	0	0
B	.012	-	17,000	0	0
C	.662	-	17,000	0	3,000
D	.059	-	1,000	0	0
E	.027	-	1,000	0	0
F	0	0	0	0	0
I	6.528	-	*	*	*
L	.049	-	0	0	0
N	.075	-	0	0	0
O	2.162	-	0	*	*
R	-	11.813	-	-	-
S	-	1.258	-	-	-
U	4.667	-	0	0	0
W	-	1.242	-	-	-

¹See plate 1 for location of sources.

*DIMP concentration in recharge varies during 1952-75 period.

the ability of the model to simulate either historical or future water-table elevations and DIMP concentrations in the aquifer. The model-calculated water-table elevations are generally within 3 ft (0.6 m) of those shown on plate 1, and all the model-generated water-level contours are located within 700 ft (210 m) of the corresponding contour shown on plate 1. The similarity between the observed DIMP concentrations and the calculated concentrations may be seen by comparing figures 2 and 3. The lack of historical data on the quantities of water discharged to each pond, the concentration of DIMP in this water, and the concentrations of DIMP in the ground water prior to 1975 contribute uncertainties to the model which are evidenced as discrepancies between the calculated and the observed data. The agreement attained between the model calculations and the observed data is sufficient, however, to consider the model calibrated and valid.

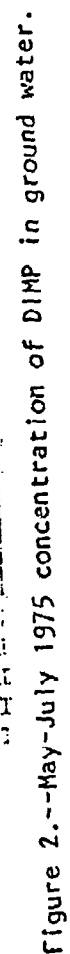
Because ground-water DIMP concentration data are not available for years prior to 1974, the model calibration is based on known concentrations at the beginning and end of the simulation period. The lack of data for intermediate checks on calibration is not a severe limitation because of the congruence between the DIMP transport model and the chloride transport model. Chloride data were available for intermediate calibration checks on the chloride model. As the hydrologic factors which affect chloride transport also affect DIMP transport, the proper calibration of the chloride model adds support to the less extensive calibration of the DIMP model.

If further DIMP-model calibration is desired, adequate concentration changes probably will have occurred in the aquifer after 2 to 3 years. A short-term calibration would then be possible if adequate data are collected in the interim. These data need to include (1) DIMP concentrations in the sources of ground-water recharge and in the aquifer, (2) the quantity of ground-water recharge from ponds and other sources, (3) water-level measurements in wells, and (4) the quantity of water pumped from wells and sumps.

The calibrated DIMP model was used to calculate the ground-water flow velocities in the alluvial aquifer (fig. 4). Velocities ranged from less than 0.1 ft/d (0.03 m/d) in the southeast part of the model area to more than 15 ft/d (0.46 m/d) near the South Platte River. When figure 4 is used in conjunction with the direction of ground-water movement shown on plate 1, the ground-water travel time between adjacent points in the aquifer may be calculated.

The model calculates annual DIMP concentrations in the ground water resulting from the estimated average concentration and rate of recharge from each pond from 1952 to 1975. By examining the spatial distribution of DIMP in the aquifer at different times it is possible to better understand the mechanism by which the DIMP contamination reached its present locations.

The DIMP concentrations in the aquifer were assumed to be zero in 1952, prior to the disposal of DIMP to the environment. During the following 4 years, DIMP was disposed of in the unlined ponds A, B, C, D, and E (pl. 1).



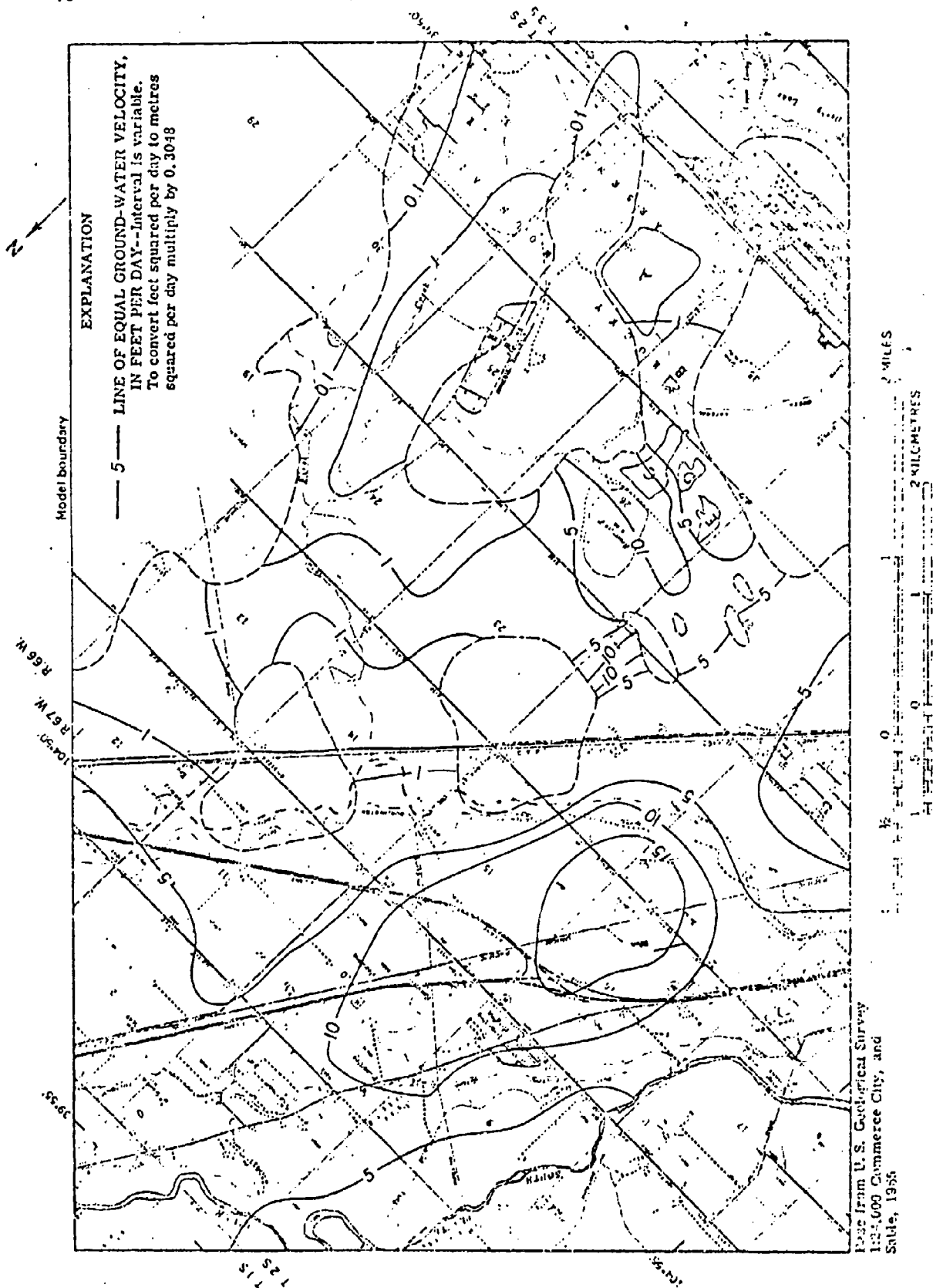


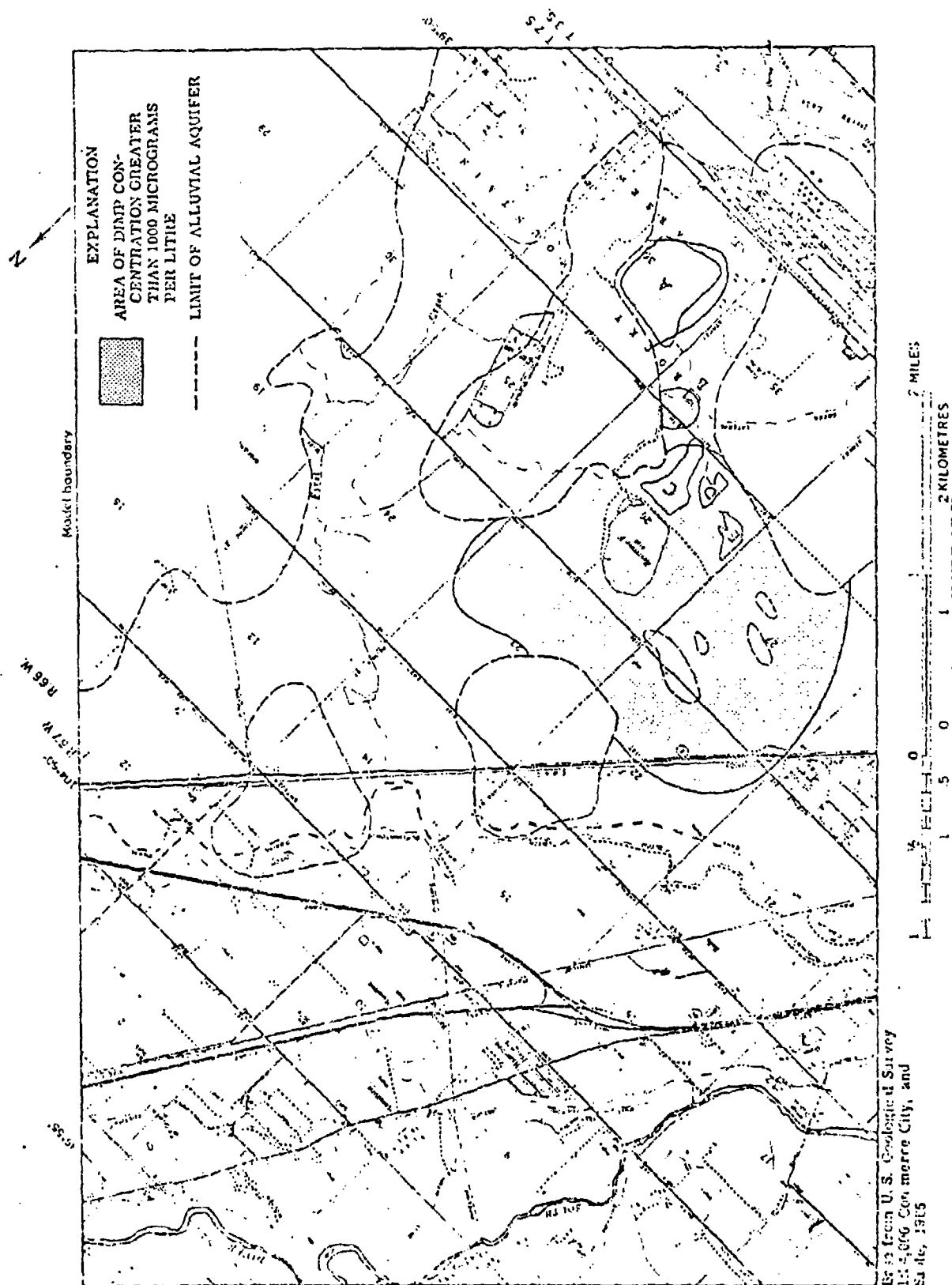
Figure 4.--Model-calculated ground-water velocities.

The resulting model calculations show DIMP concentrations in excess of 1,000 $\mu\text{g/l}$ (micrograms per litre) in the areas shown on figure 5. After the completion of the lined Reservoir F in 1956, it is assumed that ground-water recharge of DIMP-contaminated water ceased. The resulting model calculations show an improvement in ground-water quality near ponds C, D, and E (fig. 5). The two zones in excess of 1,000 $\mu\text{g/l}$ near ponds A and B had merged by 1960 and remained near this location through subsequent years due to the low ground-water velocities in the area. By examining figures 5 through 9 it can be seen that the main part of the contaminated ground water moves from ponds C, D, and E to the South Platte River through the aquifer to the west of Reservoir F. The model indicates that by 1972 (fig. 9) this plume was no longer present in concentrations greater than 1,000 $\mu\text{g/l}$. However, DIMP concentrations in excess of 1,000 $\mu\text{g/l}$ persist from 1956 to 1975 northeast of Reservoir F due to the lower ground-water velocities in this area.

Ground-water discharge occurs at springs and seeps along a reach of First Creek from near 96th Avenue to the O'Brian Canal. The model indicated that a maximum DIMP concentration of about 2 $\mu\text{g/l}$ would occur in the canal as a result of First Creek water discharging into the canal. This is consistent with the 2.5 $\mu\text{g/l}$ DIMP found in two samples of water from Barr Lake (the terminus of the O'Brian Canal).

When no additional DIMP input after 1956 is assumed in the model, the 1975 calculations show an area larger than 1 mi^2 (3 km^2) near ponds C, D, and E, and Reservoir F with a DIMP concentration less than 5 $\mu\text{g/l}$. The DIMP concentrations observed in May and June 1975 in this area range between about 300 and 3,000 $\mu\text{g/l}$. This discrepancy suggests that an additional input of DIMP has occurred in this area. The change in DIMP concentration with time, shown in figure 10, indicates that ground water with a high DIMP concentration has moved into the area of well 41 during the period of record, August 1974 to August 1975. (Locations of wells discussed are shown on fig. 2.) The high-concentration water moved into well 141 prior to the start of the record in January 1975. This could indicate that well 141 is closer to the source of contamination than is well 41. The concentrations found in well 127 suggest that: (1) The contaminant arrived at this well at about the same time as at well 41, and (2) well 127 is located near the lateral edge of the degraded zone. The relatively low concentrations of DIMP found in wells 145 and 129 (fig. 2) indicate that ground water with DIMP concentrations as high as those in wells 41 and 141 does not appear to be moving downgradient from ponds A or B. The direction of ground-water movement shown on plate 1, in addition to the above data, suggest that the source of the recent DIMP input is in the southern one-half of sec. 26, T. 2 S., R. 67 W. There are insufficient data to determine the mechanism responsible for the possible recent DIMP input or the exact location of the source. Possibilities to be considered include:

1. Percolation in ponds C, D, or E of surface runoff from ponds A or B.
2. Induced recharge of DIMP-contaminated water from permeable strata in the underlying Dawson Formation.



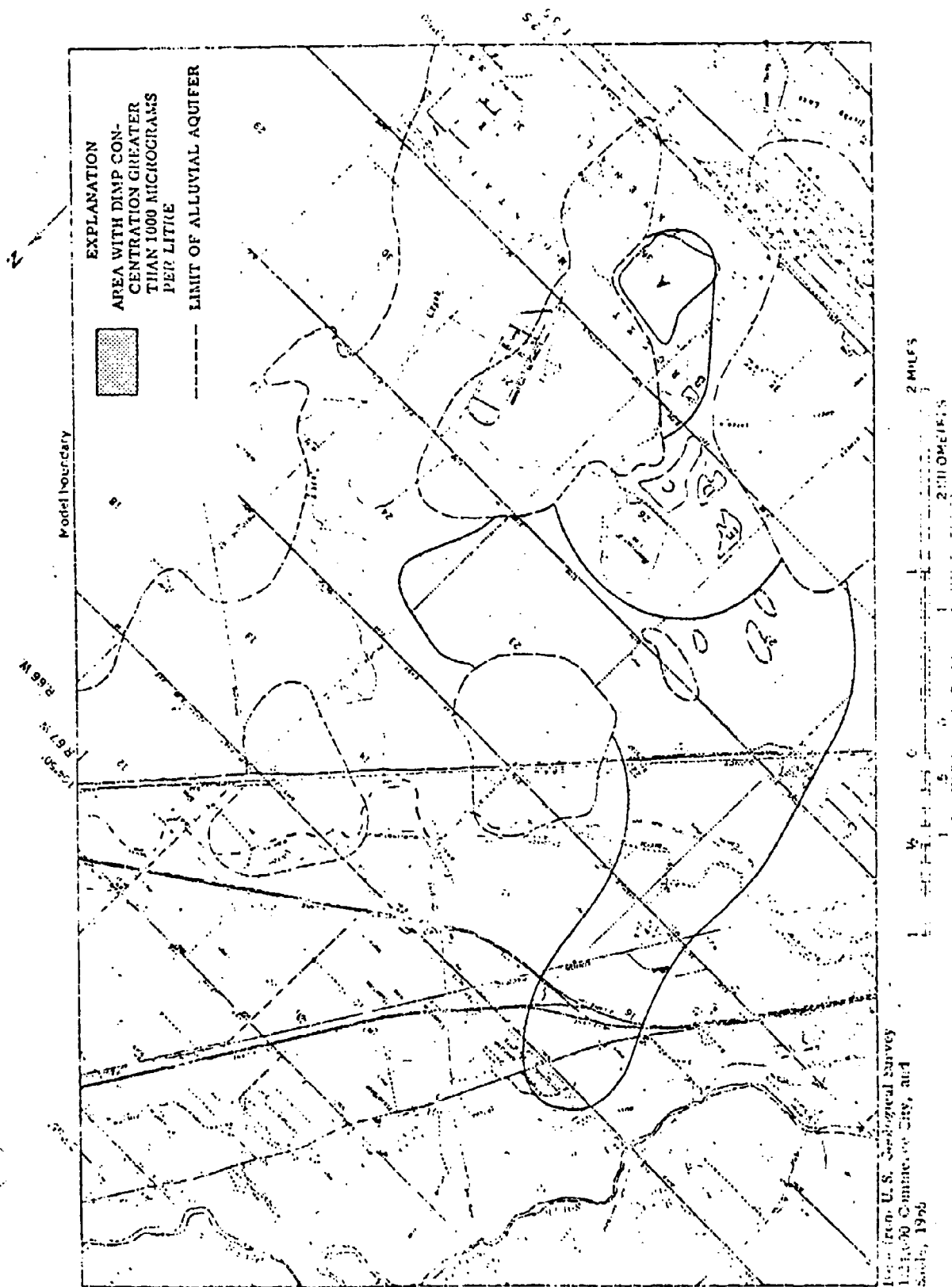


Figure 6.--Model-generated 1960 concentration of DIMP in ground water.

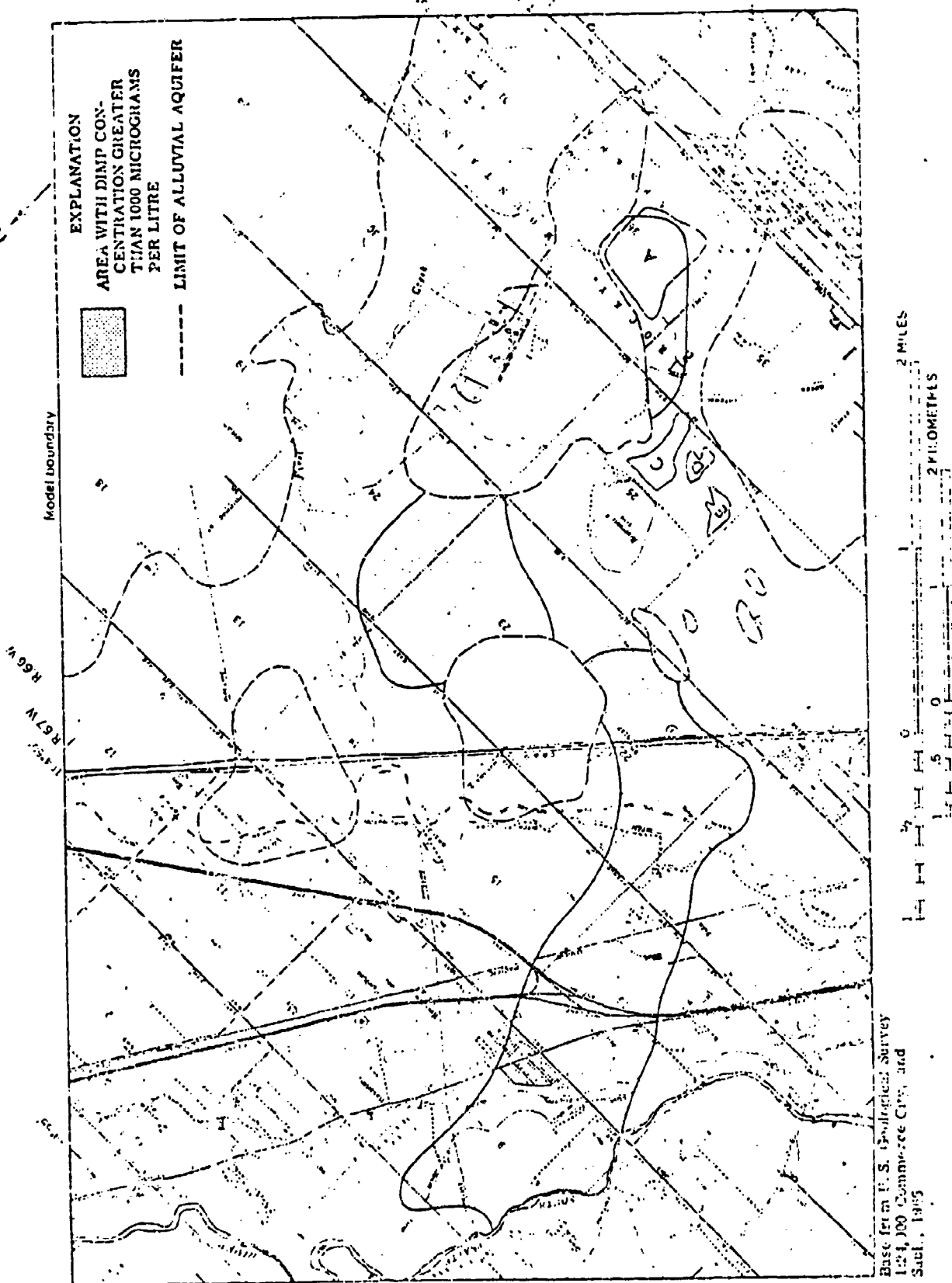


Figure 7.--Model-generated 1964 concentration of DIMP in ground water.

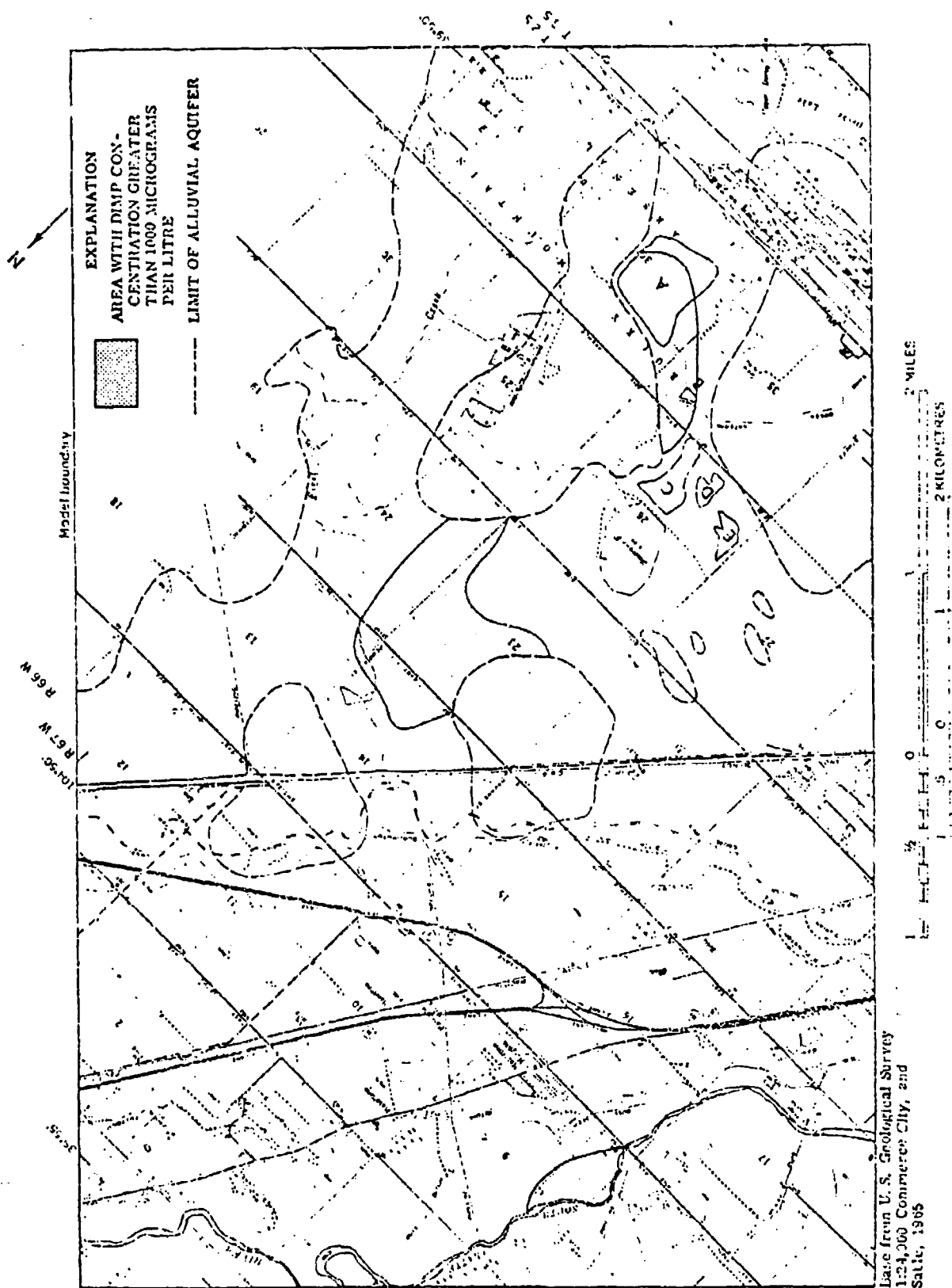


Figure 8.--Model-generated 1968 concentration of DIMP in ground water.

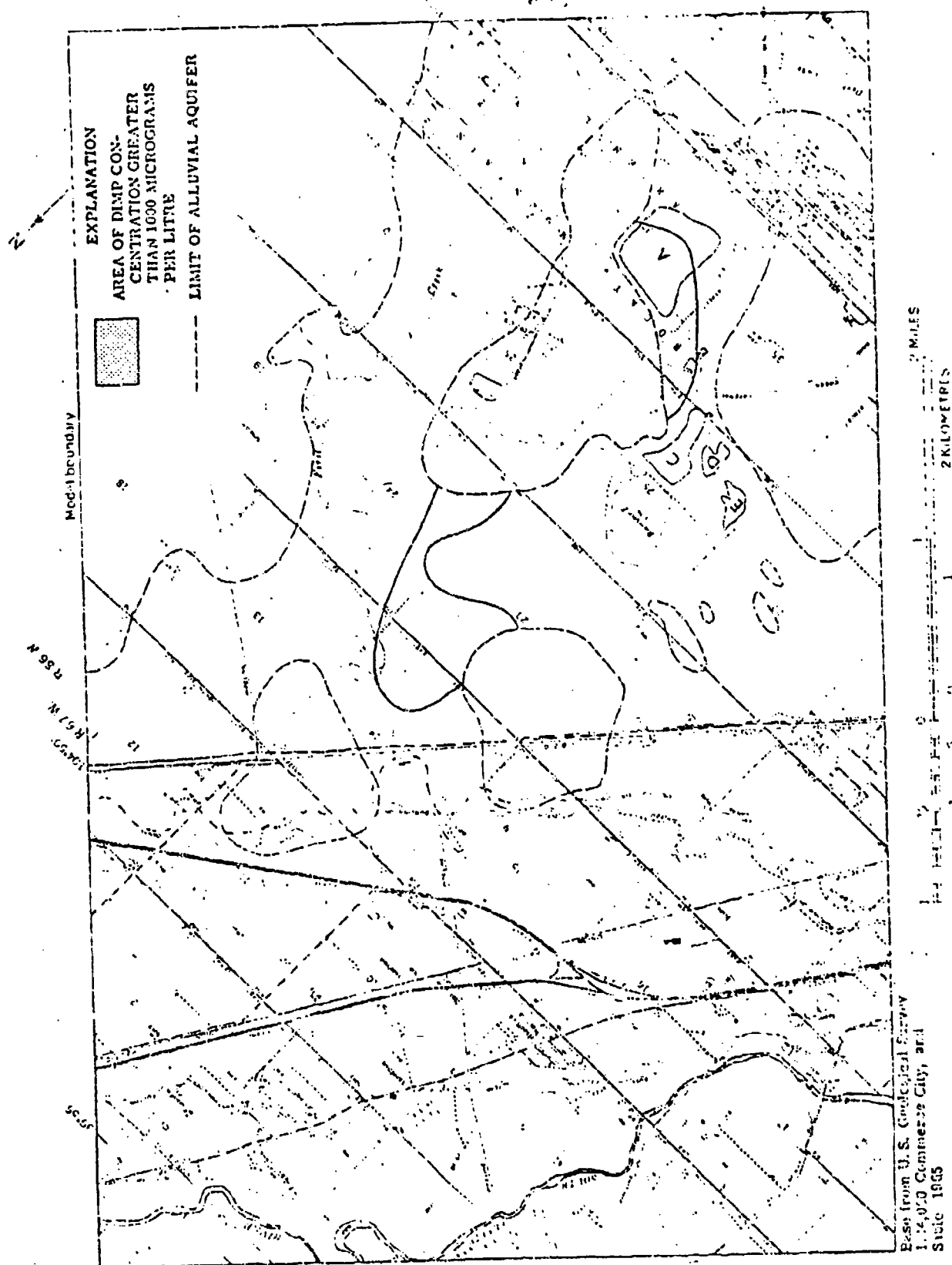


Figure 9.--Model-generated 1972 concentration of DIMP in ground water.

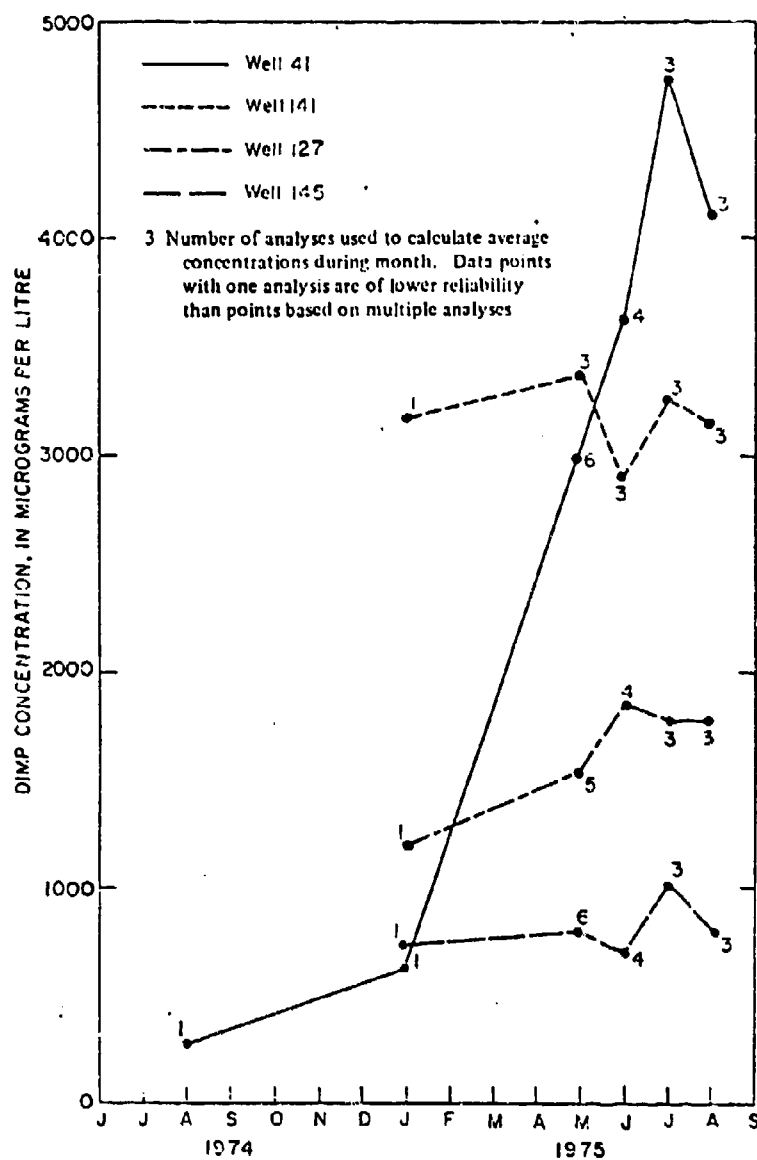


Figure 10.--Change in DIMP concentration with time in selected wells.
(See figure 2 for location of wells.)

3. Release of DIMP previously concentrated by evaporation from the soil of the unsaturated zone.

4. A leak in the liner or discharge pipeline to Reservoir F; however, there are no conclusive water-quality data to indicate that a leak in the liner of Reservoir F exists. It was found by use of the model that a DIMP input from pond C, of 1-year duration at a concentration of 3,000 ug/l, was adequate to reasonably simulate the 1975 observed concentrations in the aquifer near ponds C, D, and E, and Reservoir F.

PRELIMINARY MODEL PROJECTIONS

The model is able to calculate future DIMP concentrations that would occur in the aquifer as a result of a given set of assumptions. The model was used to calculate the DIMP concentrations that would occur during the next 20 years if no significant changes occurred in the aquifer system or the operational practices of the ponds. Model assumptions were that: (1) The future quantities of water recharged from ponds A through E would not differ from the historic average, (2) the DIMP concentration of this water would be zero, (3) the aquifer would remain in a steady-flow condition in the future, and (4) the pattern and quantity of irrigation recharge and pumpage would not change over the next 20 years. The observed 1975 DIMP concentrations in the aquifer (fig. 2) were used as the initial concentration of the model aquifer for 1975. The resulting model-calculated concentrations for 1985 and 1995 are shown on figures 11 and 12. By comparing figures 2, 11, and 12 the changes in DIMP concentration between 1975, 1985, and 1995 may be seen. The model indicates that the high DIMP concentrations near pond C in 1975 will have an adverse effect on the concentrations in the aquifer between pond C and the South Platte River. In 1985, DIMP concentrations in excess of 20 ug/l probably will occur in this area. By 1995 this zone of increased concentration probably will have decreased in size and no longer extend to the South Platte River. A general trend of improving water quality is evident in most of the remaining area of contamination from 1975 to 1995.

A second set of conditions to be evaluated by use of the model involved the installation of a barrier to the movement of ground water between ponds B and C. The model assumptions for this condition were the same as before except that an impermeable barrier was assumed to halt all underflow moving past the location of the barrier. No water-level changes occurred upgradient of the barrier because it was assumed that any water collecting behind the barrier would be artificially removed from the hydrologic system. Water levels in the aquifer immediately downgradient from the barrier declined to the extent that the aquifer was dewatered. The resulting 10- and 20-year model projections are shown on figures 13 and 14. A comparison of figures 2, 13, and 14 shows the changes in DIMP concentrations from 1975 to 1995. The high concentrations near pond C in 1975 still have an adverse effect on the 1985 concentrations in the aquifer between the pond and the South Platte River. The slower improvement in quality in this area by 1995 than was shown on figure 12 is due to the reduced ground-water velocity produced by the loss of underflow

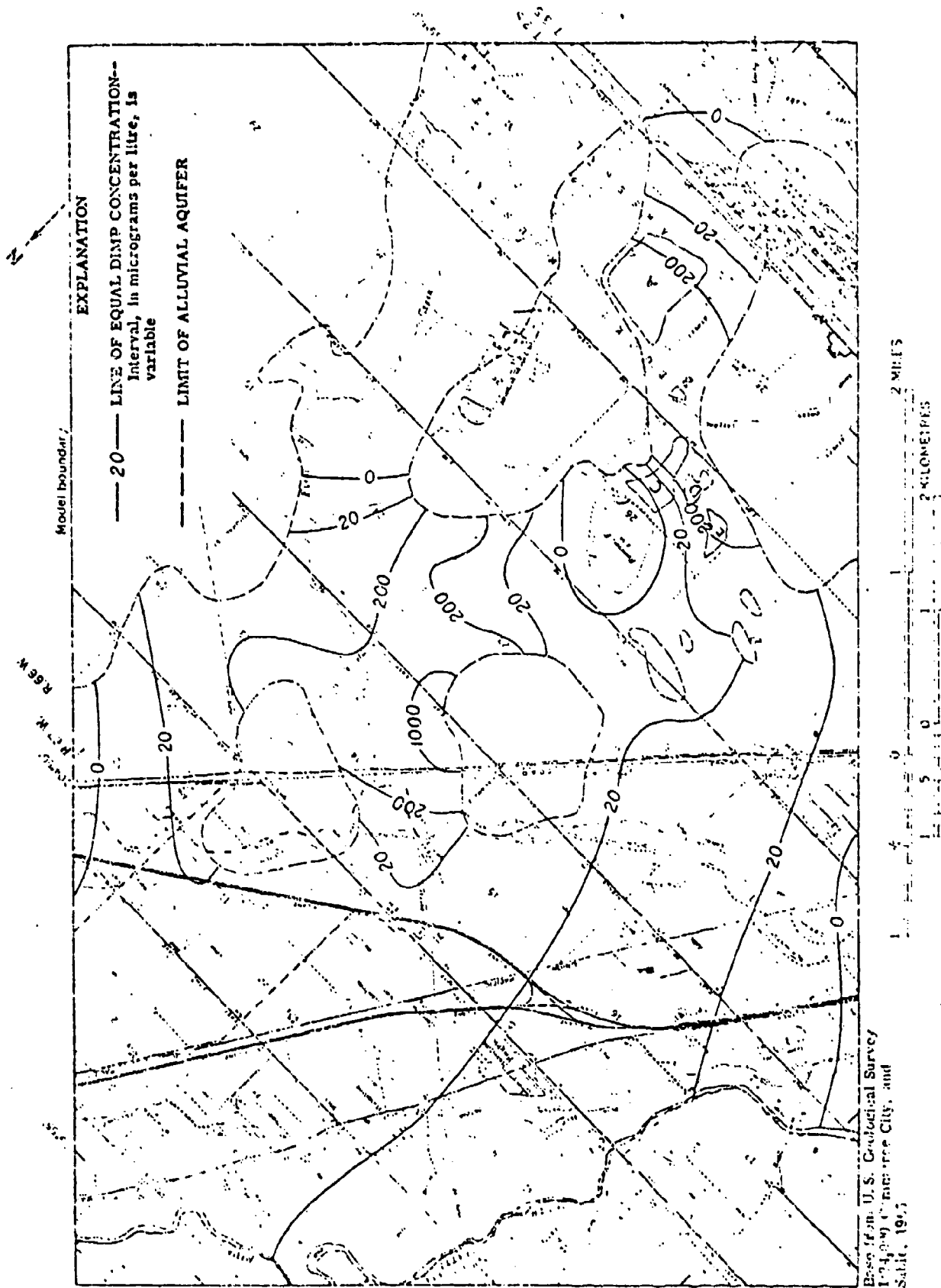


Figure 11.--Model-generated 1985 concentration of DIMP in ground water.

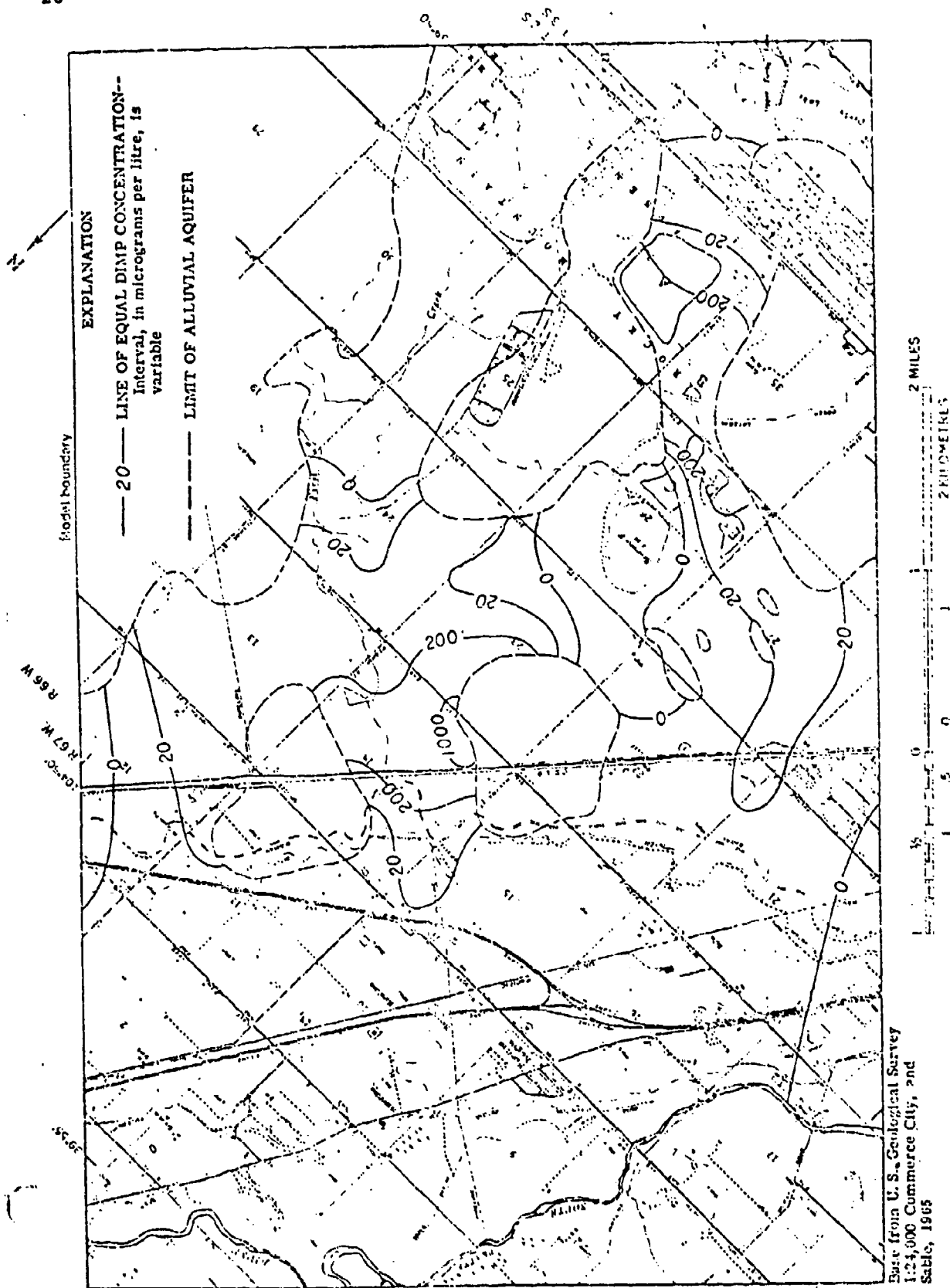


Figure 12.--Model-generated 1995 concentration of DIMP in ground water.

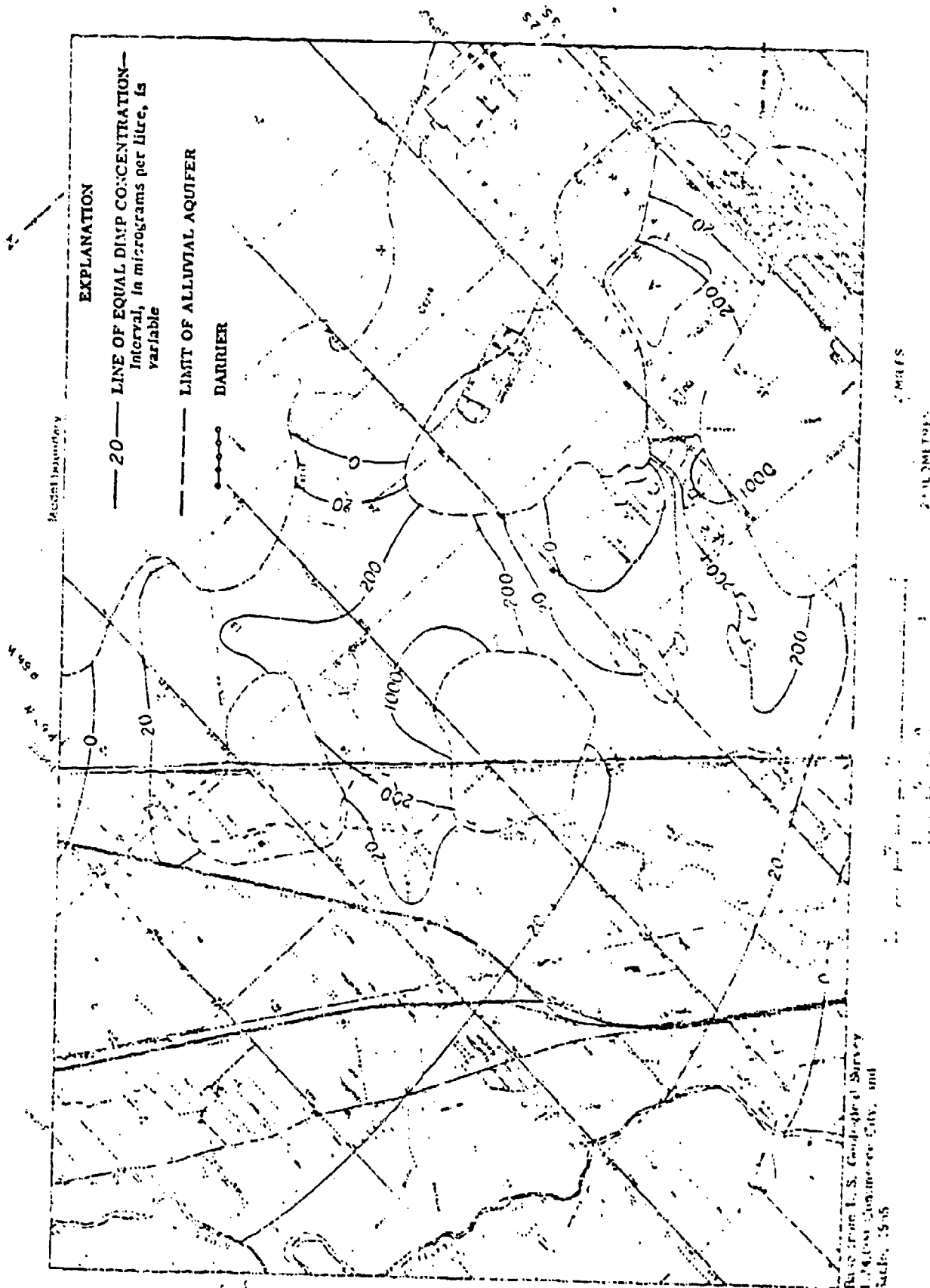


Figure 13.--Model-generated 1985 concentration of DIMP in ground water with ground-water barrier south of pond C.

past the barrier. It should be noted that the reduction of underflow through an area will retard the movement of ground water but will do little to change the DIMP concentration of the water.

MANAGEMENT OBJECTIVES

Before a "best" water-quality management procedure can be determined, the desired objective needs to be firmly established by the Rocky Mountain Arsenal, the Colorado Department of Health, and other concerned parties. This objective will strongly influence the choice of management procedures to be used. Two hypothetical examples can be used to illustrate this point. In the first example, the objective would be to reduce the DIMP concentrations in the alluvial aquifer both on and off the arsenal as rapidly as possible. In the second example, the objective would be to reduce the amount of DIMP reaching the South Platte River and the surrounding alluvial aquifer outside the arsenal. A water-quality management procedure that might be effective in meeting the first example objective would be to increase the quantity of fresh-water recharge to the aquifer on the arsenal. This would increase the ground-water velocities in the aquifer and move the DIMP-contaminated water out of the area more rapidly. However, this management procedure could be detrimental if the second example objective were to be used. A management procedure that would be better suited to the second objective would be to cease all artificial recharge on the arsenal and pump numerous wells in the degraded plume near the arsenal boundary. The two hypothetical examples require drastically different management procedures, but both have objectives which would lead to an improvement in ground-water quality.

SUMMARY

The results presented in this report complete the work on the Phase I DIMP model. The model has been developed and adequately calibrated by comparing model calculations with observed field data. The model is capable of calculating DIMP concentrations in ground water that would occur in response to a variety of ground-water management alternatives. Two examples have been given to illustrate how different water-quality management procedures can affect the DIMP concentrations in the aquifer over a 20-year period. The examples indicated that the addition of a barrier to the movement of ground water located south of pond C would reduce the quantity of water moving through the downgradient parts of the aquifer, thereby reducing the ground-water velocities in these areas. As a result, the DIMP concentrations in ground water would be slightly higher at the end of 20 years with the barrier than they would be without the barrier. Model runs using different management alternatives, different assumptions about the ground-water flow system, or different time periods are also possible. The exact objective of the ground-water quality management must be firmly established before an optimum plan of action can be determined, as very similar objectives can require drastically different plans of action.

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